Colloid stability ٣

Kinetics of coagulation

Lyophobic dispersions are never stable in the thermodynamic sense, but exhibit some degree of instability. From a practical point of view, the word 'stable' is often loosely used to describe a dispersion in which the coagulation rate is slow in relation to its required 'shelf life'.

The rate at which a sol coagulates depends on the frequency with which the particles encounter one another and the probability that their thermal energy is sufficient to overcome the repulsive potential energy barrier to coagulation when these encounters take place.

The rate at which particles aggregate is given by

$$-\frac{dn}{dt} = k_2 n^2$$

Where n is the number of particles per unit volume of sol at time t, and $k2$ is a second-order rate constant, Integrating, and putting n - n_o at $t = 0$,

gives $\dfrac{1}{n} - \dfrac{1}{n_o} = kt$ \qquad (16)

During the course of coagulation k_2 usually decreases, and sometimes an equilibrium state is reached with the sol only partially coagulated. This may be a consequence of the height of the repulsion energy barrier increasing with increasing particle size. In experimental tests of stability theories it is usual to restrict measurements to the early stages of coagulation (where the aggregating mechanism is most straightforward), using moderately dilute sols.

The particle concentration during early stages of coagulation can be determined directly, by visual particle counting, or indirectly, from turbidity (spectrophotometric or light scattering) measurements. If necessary, coagulation in an aliquot of sol can be halted prior to

examination by the addition of a small amount of a stabilizing agent, such as gelatin. The rate constant k_2 is given as the slope of a plot of l/n against t.

In most colloid stability studies, coagulation rates are measured, as far as possible, under *perikinetic* (non-agitated) conditions, where particle-particle encounters are solely the result of Brownian motion. Particle aggregation under *orthokinetic* (agitated) conditions is of technological importance. Agitation increases the particle flux by a factor which depends on the third power of the collision diameter of the particles. With large particles, such as in emulsions, orthokinetic aggregation can occur at up to as much as 10^4 times the perikinetic rate; but, with particles at the lower end of the colloidal size range, stirring has relatively little effect on their rate of aggregation.

The potential energy barrier to coagulation can be reduced to zero by the addition of excess electrolyte, which creates a situation in which every encounter between the particles leads to permanent contact. The theory of rapid coagulation was developed by Smoluchowski. For a monodispersed sol containing spherical particles, and considering only the aggregation of single particles to form doublets

$$n = \frac{n_o}{(1 + 8\pi\, Dan_o t)} \qquad (17)$$

Where a is effective radius of the particles and D is the diffusion coefficient. Substituting $D = kT/6\eta\pi a$ and combining equations (16) and (17) gives $k_2^0 = 4kT/3\eta$ $\qquad (18)$ where k_2^0 is the rate constant for diffusion-controlled coagulation.

For a hydrosol at room temperature, the time $t_{1/2}$ in which the number of particles is halved by diffusion-controlled coagulation is calculated from the above equations to be of the order of $10^{11}/n_o$ seconds, if n_o is expressed in the unit, particles cm^{-3}. In a typical dilute hydrosol, the

number of particles per cm3 may be about 10^{10}- 10^{11}, and so, on this basis, $t_{1/2}$ should be of the order of a few seconds. Rapid coagulation is, in fact, not quite as simple as this, because the last part of the approach of two particles is *(a)* slowed down because it is difficult for liquid to flow away from the narrow gap between the particles, and *(b)* accelerated by the van de Waals attraction between the particles. Lichtenbelt and co-workers have measured rapid coagulation rates by a stopped-flow method and found them, typically, to be about half the rate predicted according to equation.

When there is a repulsive energy barrier, only a fraction *1/W* of the encounters between particles lead to permanent contact. *W* is known as the stability ratio $W = k_2^o / k_2$ (19)

A theoretical expression relating the stability ratio to the potential energy of interaction has been derived by Fuchs

$$W = 2a \int_{2a}^{\infty} \frac{\exp(V / kT)}{R^2} dR \qquad (20)$$

Theoretical relationships between the stability ratio and electrolyte concentration can be obtained by numerical solution of this integral for given values of *A* and ψ_d. Figure 8.7 shows the results of calculations for 1-1 and 2-2 electrolytes. For constant ψ_d, a linear relationship between log *W* and log *c* is predicted for practically the whole of the slow coagulation region.
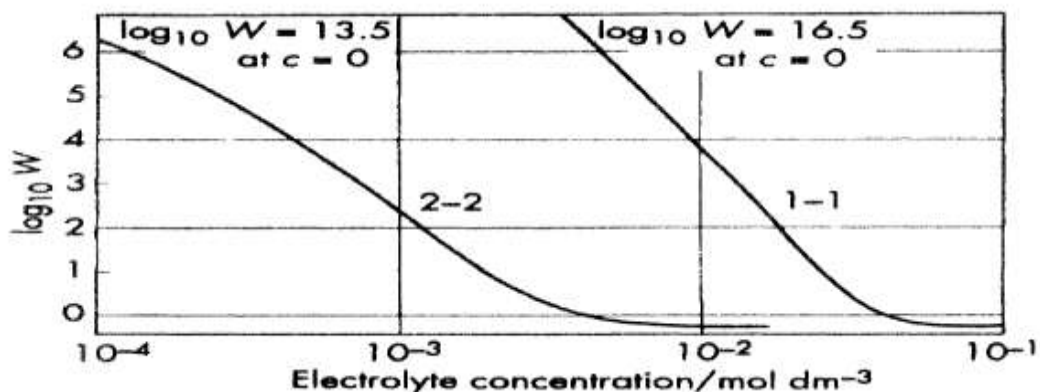
Figure 8.7 Theoretical dependence of stability ratio on electrolyte concentration calculated from equation (2) for $a = 1^{-8}$ m, $A = 2 \times 10^{19}$ J and $\psi_d = 76.8$ mV = *3kT/e*. At high electrolyte concentrations $W < 1$ owing to coagulation being accelerated by van der Waals attractive forces (reduced flow rate in the narrow interparticle gap has not been allowed for

An alternative approach (which is more convenient, but more approximate) is that of Reerink and Overbeek, who have combined an approximate form of equation (20), with equations (7) and (10) to derive a theoretical expression which also predicts a linear relationship between log W and log c at constant ψ_d. For a temperature of 25°C and with the particle radius expressed in meters, the resulting equation takes the form

$$W = \frac{1}{2\kappa a}\exp\left[\frac{V_{\max}}{kT}\right] \quad , \log W = cons\tan t - 2.06x10^9\left(\frac{a\gamma^2}{z^2}\right)\log c \quad (21)$$

According to this approximation, d log W/d log c for the example of $a = 10^{-8}$ m and $\psi_d = 3kT/e$ chosen in Figure 8.7 is equal to 9 for 1-1 electrolytes and 4.8 for 2-2 electrolytes, whereas the more exact calculations via equation (20) give slopes of 7 and 4.5, respectively. Coagulation rates have been measured as a function of electrolyte concentration for a number of Sols and the predicted linear relationship between log W and log c in the slow-coagulation region seems to be well confirmed. In addition, the experimental values of d log W/d log c, although somewhat variable, are of the right order of magnitude compared with theoretical slopes.

Figure 8.8 shows some interesting results which have been obtained by Fairhurst and Smith for the coagulation of silver iodide hydrosols at various pi values. As the pi is decreased (and the potential ψ_o becomes

more negative) the slope d log *W/d* log c and the critical coagulation concentration (which is the concentration which corresponds to an arbitrarily chosen low value of *W)* increase, as expected, until a pI of about 6 is reached. However, as the pI is reduced below 6, d log *W/d* log *c* and the critical coagulation concentration decrease. This apparently anomalous observation (and the corresponding maximum in the zeta potential curve - Figure 7.4) may be a consequence of the discreteness of charge effect
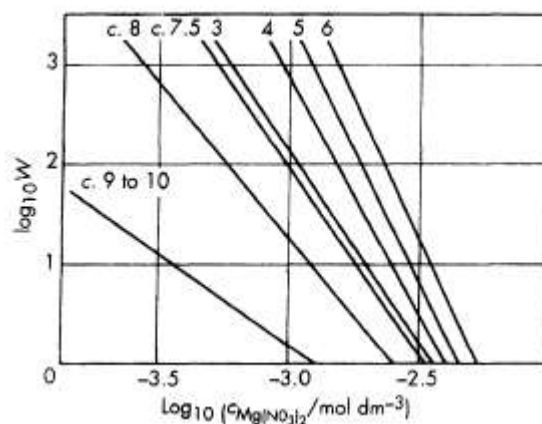

Figure 8.8 Plots of log *W* versus log c for coagulation of Agl sols at various pi values by magnesium nitrate206

Experimental data are generally not in accord with the theoretical prediction in equation (21) regarding particle size. For example, Ottewill and Shaw204 found no systematic variation in d log *W/d* log *c* for a number of monodispersed carboxylated polystyrene latex dispersions with the particle radius ranging from 30 nm to 200 nm. This problem still remains unresolved.

Peptization

Peptization is a process in which dispersion is achieved (with little or no agitation) by changing the composition of the dispersion medium.

Methods of Peptization include addition of polyvalent co-ions (e.g. polyphosphate ions to a negatively charged coagulated dispersion), addition of surfactants, dilution of the dispersion medium and dialysis. In

each case, V_R is modified so as to create a potential energy maximum (see Figures 8.2-8.4) to act as a barrier against recoagulation.

Simple consideration of lyophobic sols in terms of their potential energy of interaction curves does not lead one to expect Peptization, since any energy barrier to coagulation would involve on the other side an even greater energy barrier to peptization. Nevertheless, peptization of lyophobic sols is possible, especially when only a short time is allowed to elapse between coagulation and peptization.

There are several possible explanations of this phenomenon,

1. Both specific adsorption (particularly, solvation) at the particle surfaces and the difficulty with which dispersion medium flows from the narrow gap between the particles may hinder particle approach to the small separation which corresponds to the primary minimum.

2. Owing to the time lag in the adjustment of potential and/or charge as particles approach or move away from one another, coagulation and peptization will occur at potentials which are, respectively, lower than and greater than the equilibrium potential.

Sedimentation volume and gelation

As the particles of dispersion usually have a density somewhat different from that of the dispersion medium, they will tend to accumulate under the influence of gravity at the bottom or at the surface. A sedimentation velocity of up to 10^{-8} m s^{-1} is usually counteracted by the mixing tendencies of diffusion and convection. Particle aggregation, of course, enhances sedimentation.

When sedimentation does take place, the volume of the final sediment depends upon the extent of aggregation. Relatively large peptized particles pack efficiently, to give a dense sediment which is difficult to re-disperse, whereas aggregated particles bridge readily and give a loose

sediment which (provided that the particles are not held together too strongly) is more easily dispersed (see Figure 8.9).

In extreme cases, the sedimentation volume may equal the whole volume, and this can lead to the paradoxical situation where a small amount of aggregating agent produces sediment while a larger amount does not. Gentle stirring usually reduces the sedimentation volume.
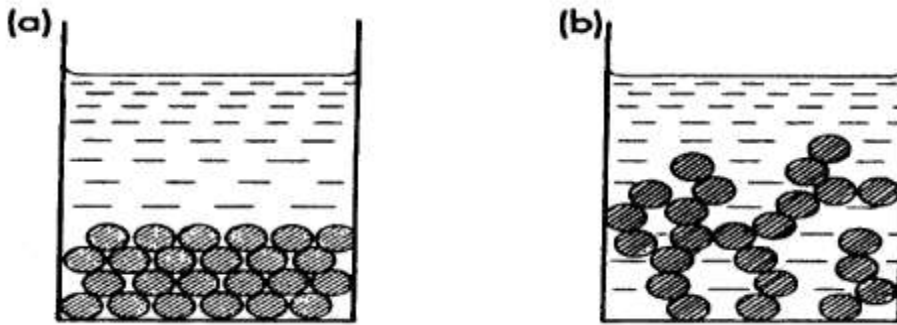

Figure 8.9 Sedimentation volumes for (a) peptised and (b) aggregated particles
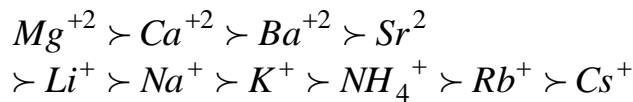
Systems containing lyophilic material
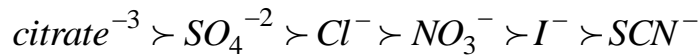
Polymer solutions

Macromolecular solutions are stabilized by a combination of electric double layer interaction and solvation, and both of these stabilizing influences must be weakened sufficiently before precipitation will take place. For example, gelatin has a sufficiently strong affinity for water to be soluble (unless the electrolyte concentration is very high) even at its isoelectric pH, where there is no double-layer interaction. Casein, on the other hand, exhibits weaker hydrophilic behavior and is precipitated from aqueous solution when the pH is near to the isoelectric point.

Owing to their affinity for water, hydrophilic colloids are unaffected by the small amounts of added electrolyte which cause hydrophobic sols to

coagulate but are often precipitated (salted out) when the electrolyte concentration is high. The ions of the added electrolyte dehydrate the hydrophilic colloid by competing for its water of hydration. The salting-out efficacy of an electrolyte, therefore, depends upon the tendencies of its ions to become hydrated. Thus, cations and anions can be arranged in the following lyotropic series of approximately decreasing salting-out power:

$$Mg^{+2} \succ Ca^{+2} \succ Ba^{+2} \succ Sr^2$$
$$\succ Li^+ \succ Na^+ \succ K^+ \succ NH_4^+ \succ Rb^+ \succ Cs^+$$

And

$$citrate^{-3} \succ SO_4^{-2} \succ Cl^- \succ NO_3^- \succ I^- \succ SCN^-$$

Ammonium sulphate, which has a high solubility, is often used to precipitate proteins from aqueous solution.

Lyophilic colloids can also be desolvated (and precipitated if the electric double layer interaction is sufficiently small) by the addition of non-electrolytes, such as acetone or alcohol to aqueous gelatin solution and petrol ether to a solution of rubber in benzene.

Dispersions containing stabilizing agents

The stability of lyophobic sols can often be enhanced by the addition of soluble lyophilic material which adsorbs on to the particle surfaces. Such adsorbed material is sometimes called a *protective agent.* The stabilization mechanism is usually complex and a number of factors may be involved.

Lyophilic stabilization is particularly important in non-aqueous systems, e.g. oil-based paints, and in systems of very high particle concentration where electrostatic stabilization is of limited effectiveness.

It is also essential in biological systems, e.g. blood, where the electrolyte concentration is often sufficiently high to render electrostatic stabilization ineffective.

Effect on electric double layer interactions

If the stabilizing agent is ionized and carries a charge of the same sign as that on the particles (e.g. anionic surfactant adsorbed on negatively charged particles), then electric double layer repulsion will be enhanced. The adsorbed stabilizing agent (even if non-ionic) will influence electrostatic interactions by causing a displacement of the Stern plane away from the particle surface; this will increase the range of electric double layer repulsion and, as such, enhance stability.

Effect on van der Waals interactions

Adsorbed layers of stabilizing agent may cause a significant lowering of the effective Hamaker constant and, therefore, a weakening of the interparticle van der Waals attraction. This effect has been considered by Void207 and by Vincent and co-workers208 in terms of the Hamaker microscopic treatment of dispersion forces.

For the interaction depicted in Figure 8.10,

$$-12V_A = F_{11}(A_{11}^{1/2} - A_{22}^{1/2}) + F_{22}(A_{22}^{1/2} - A_{33}^{1/2})^2 \\ + F_{12}(A_{11}^{1/2} - A_{22}^{1/2})(A_{22}^{1/2} - A_{33}^{1/22})$$
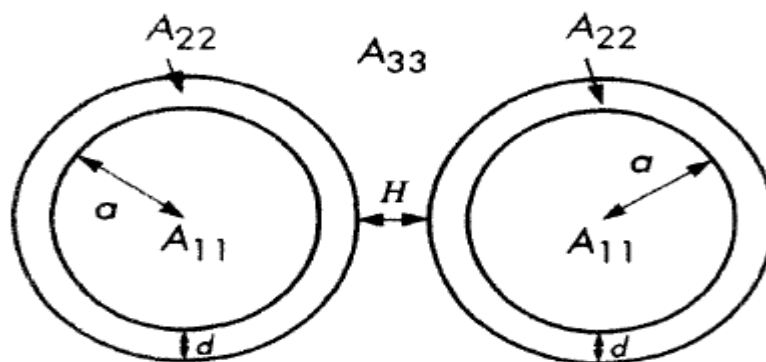

Figure 8.10

Where

$$f = \left[\frac{y}{x^2xy+x} + \frac{y}{x^2+xy+x+y} + 2\ln\left(\frac{x^2xy+x}{x^2+xy+x+y}\right) \right]$$

With x and y defined as:

$$for\, F_{11} \quad x=(H+2d)/2a \quad y=1$$
$$for\, F_{22} \quad x=H/2(a+d) \quad y=1$$
$$for\, F_{13} \quad x=(H+d)/(2a+d) \quad y=(a+d)/2a \qquad (22)$$

Steric stabilization

The stability of much 'protected' colloidal dispersion cannot be explained solely on the basis of electric double layer repulsion and van der Waals attraction; other stabilizing mechanisms must be investigated. 'Steric stabilization' is a name which is used (somewhat loosely) to describe several different possible stabilizing mechanisms involving adsorbed macromolecules. These include the following:

1. An encounter between particles could involve desorption of stabilizing agent at the point of contact. Since adsorption is a spontaneous process, A G_{ads} is negative and A G_{das} positive. This positive free energy of desorption corresponds to particle-particle repulsion and enhanced stability. However, for polymeric material, adsorption and desorption processes tend to be slow compared with the time of a typical particle-particle encounter" and so, in such cases, the attainment of a 'primary minimum' coagulated condition is unlikely.

2. When particles collide, their adsorbed layers may be compressed without penetrating into one another. This 'denting' mechanism will reduce the configurations available to the adsorbed polymer molecules; therefore, there will be a decrease in entropy and an increase in free energy, and stability will be enhanced by an elastic effect. However, it is likely that this mechanism is not significant in practice.

3. The adsorbed layers between the particles may interpenetrate and so give a local increase in the concentration of polymer segments. Depending on the balance between polymer-polymer and polymer dispersion medium interactions, this may lead to either repulsion or attraction by an osmotic mechanism. Enthalpic and entropic changes will be involved. If interpenetration takes place to a significant extent, elastic repulsion will also operate.

Steric stabilizers are usually block copolymer molecules (e.g. poly (ethylene oxide) surfactants), with a lyophobic part (the 'anchor' group) which attaches strongly to the particle surface, and a lyophilic chain which trails freely in the dispersion medium. The conditions for stabilization are similar to those for polymer solubility outlined in the previous section. If the dispersion medium is a good solvent for the lyophilic moieties of the adsorbed polymer, interpenetration is not favored and interparticle repulsion results; but if, on the other hand, the dispersion medium is a poor solvent, interpenetration of the polymer chains is favored and attraction results. In the latter case, the polymer chains will interpenetrate to the point where further interpenetration is prevented by elastic repulsion.

The free energy change which takes place when polymer chains interpenetrate is influenced by factors such as temperature, pressure and solvent composition, The point at which this free energy change is equal to zero is known as the θ (theta)-point and such a solvent is called a θ-solvent. More formally, a θ-point is defined as one where the second virial coefficient of the polymer chains is equal to zero. It can be determined by light scattering and by osmometry.

The positive ΔG for polymer chain interpenetration which leads to steric stabilization is given in terms of the corresponding enthalpy and entropy changes by $\Delta G = \Delta H - T\Delta S$, and therefore, stabilization could be the

result of a positive ΔH and/or a negative ΔS. A positive ΔH would reflect the release of bound solvent from the polymer chains as they interpenetrate and a negative ΔS would reflect loss of configurational freedom as the polymer chains interpenetrate. If ΔH is positive and ΔS negative, the dispersion will be sterically stabilized at all accessible temperatures; however, if ΔH and ΔS are both positive, the dispersion should flocculate on heating above the θ- temperature (enthalpic stabilization), whereas if ΔH and ΔS are both negative, the dispersion should flocculate on cooling below the θ-temperature (entropic stabilization).

These effects have been observed for both aqueous and non-aqueous media and good correlation between the point of incipient flocculation and the θ-temperature is well established. The transition from stability to instability usually occurs over a very narrow temperature range (1 or 2 K). Enthalpic stabilization tends to be the more common in aqueous media and entropic stabilization the more common in non-aqueous media. Owing to the elastic effect, aggregation into a deep primary minimum does not take place (as is possible with lyophobic sols) and re-dispersion takes place readily on reverting to better than θ-solvent conditions,

Several quantitative theories of steric stabilization have been developed over the last few decades.

The forces between sterically stabilized particles have been measured with a compression cell, and have been shown (as expected in the light of the foregoing discussion) to be short-range, with a range comparable with twice the contour length of the lyophilic chains. For sterically stabilized systems the total interaction energy can be written as

$$V = V_R + V_A + V_s \qquad (23)$$

and potential energy diagrams will be as schematically depicted in Figure 8.11, with entry into a deep primary minimum made virtually impossible by the steric interactions.
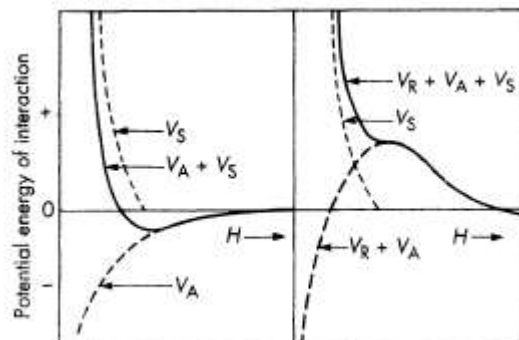

Figure 8.11 Schematic interaction energy diagrams for sterically stabilized particles: (a) in the absence of electric double layer repulsion $(V = V_A + V_s)$, (b) with electric double layer repulsion $(V = V_R + V_A + V_s)$

Sensitization

In certain cases, colloidal dispersions are made more sensitive to aggregation by the addition of small quantities of materials which, if used in larger amounts, would act as stabilizing agents. Several factors may contribute to such observations:

1. If the sol particles and the additive are oppositely charged, sensitization results when the concentration (and adsorption) of the additive is such that the charge on the particles is neutralized, whereas stabilization results at higher concentrations because of a reversal of the charge and increasing steric effects.

2, At low concentrations, surface-active additives may form a first adsorbed layer on the sol particles with the lyophobic part orientated outwards, thus sensitizing the sol. At higher concentrations a second, oppositely orientated, layer would then give protection.

3. Long-chain additives, such as gelatin, can sometimes bring about a rather loose flocculation by a bridging mechanism in which the molecules are adsorbed with part of their length on two or more particles. Such flocculation normally occurs over a narrow range of additive concentrations; at high concentrations protective action is obtained, since bridging can occur only through particle collisions under conditions where further adsorption of the additive is possible.

Dispersions of hydrophilic particles in oil media can be flocculated by traces of water, which form thin interconnecting films between the particles.

Another interesting phenomenon is that of depletion flocculation. This can be observed with dispersions (e.g. lattices) which contain inert additives, such as free polymer, non-ionic surfactant or even small (e.g. silica) particles. As the latex particles approach one another, the gaps between them become too small to accommodate the above additives, but the kinetic energy of the particles may be sufficient to enable them to be expelled from the gap; i.e. a 'de-mix' occurs, for which AC is positive. When this 'de-mix' has been achieved, an osmotic situation exists in which the remaining pure dispersion medium will tend to flow out from the gap between the particles in order to dilute the bulk dispersion medium, thus causing the particles to flocculate.

Stability control

Particle aggregation and sedimentation volume are important in many practical situations, as illustrated by the following examples.

1. *Agricultural soil. It* is necessary to maintain agricultural soil in a reasonably aggregated state in order to achieve good aeration and drainage, and treatment with coagulants, such as calcium salts (lime or gypsum) or organic polyelectrolyte (so-called soil conditioners), is common practice. An extreme example of the effect of soil peptization

occurs when agricultural land is flooded with sea-water. The calcium ions of the naturally occurring clay minerals in the soil exchange with the sodium ions of the seawater. Subsequent leaching of the sodium ions from the soil by rain-water leads to peptization and the soil packs into a hard mass which is unsuitable for plant growth. Conversely, water seepage from reservoirs can be reduced by initial flooding with sea-water,

2. *Oil well drilling.* In the drilling of oil wells a drilling mud (usually a bentonite clay suspension) is used *(a)* as a coolant, *(b)* for removing the cuttings from the bore-hole and (c) to seal the sides of the bore-hole with an impermeable filter cake. The pumping and sealing features of this operation are most effective if the drilling mud is peptized; however, a certain amount of mud rigidity is required to reduce sedimentation of the cuttings, especially during an interruption of circulation. These opposite requirements are somewhat reconciled by maintaining the drilling mud in a partially coagulated, thixotropic state. If the drilling mud stiffens, partial re-dispersion can be effected by the addition of a small amount of a peptizing agent, such as a polyphosphate. The plate-like particles of clays often have negatively charged faces and positively charged edges when in contact with aqueous media, and aggregate quite readily by an edge-to-face mechanism to form a gel structure, even at moderately low clay concentrations18. The main function of the polyphosphate is to reverse the positive charge on the edges of the clay particles. The relatively small edge area makes this process economically attractive.

3. *Sewage treatment and water purification.* Industrial waste water and domestic sewage contains a variety of particulate matter and surfactant (mostly anionic). The zeta potentials of the particles are usually in the range -10 to -40 mV. Considerable purification can be effected by the

addition of small amounts of sodium hydrogen carbonate plus aluminum sulphate and agitating the mix. The aluminum ions are hydrolyzed to give a polymeric hydrous oxide gel network in which the suspended particles become entrapped and bound together by a bridging mechanism. The pH is adjusted to near pH 6 to give a slightly positive zeta potential (+5 mV). At this zeta potential, electrostatic stabilization is insignificant, but a significant removal of anionic surfactant by adsorption on to the positively charged floes takes place. In the final stage of water purification, most -of the remaining particulate matter can be removed by the addition of a few parts per million of high molecular mass polyacrylamide, again by a bridging mechanism.

4. *Paints.* The particles in pigmented paints are often large enough to settle even when peptized; therefore, it is desirable that they should be aggregated to a certain extent to facilitate re-dispersion. Some other practical situations where particle aggregation is important include the precipitation of colloidal mud at the mouth of a river due to the salinity of the sea-water exceeding the critical coagulation concentration, land (e.g. mountainside) stability, building and road foundations, the retention of a porous structure in filtration, mineral processing and paper making. Control of particle aggregation is also of primary importance in adhesives, inks, Pharmaceuticals, cosmetics, foodstuffs and lubricants.